

ESI for

**Transition Metal Doping Activated Basal-Plane Catalytic Activity of
Two-Dimensional 1T'-ReS₂ for Hydrogen Evolution Reaction: A
First-Principles Calculation Study**

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The calculated details of LDOS of in-plane S atoms and edge S atoms

To investigate the local density of states (LDOS) of in-plane S atoms and edge S atoms, we built a ReS₂ nanoribbons by cutting from a periodic monolayer ReS₂ along its diamond-shaped (DS) chains direction, with S atoms on both edges, as shown in Fig. S1. A one-dimensional periodic boundary condition is used along with the growth direction, vacuum layers of at least 10 Å are incorporated along the nonperiodic direction to ensure decoupling between neighboring images.

The GGA of the PBE exchange-correlation functional was implemented. The cutoff energy for the plane-wave basis set was 400 eV. Self-consistency was reached once energy difference between two consecutive steps was less than 1.0×10^{-5} eV, and the Hellman-Feynman forces acting on each atom was smaller than 0.01 eV/Å. The Monkhorst-Pack k -point was set to $9 \times 1 \times 1$ for the first Brillouin zone integration in geometry optimization and increased to $31 \times 1 \times 1$ in electronic structure calculations.

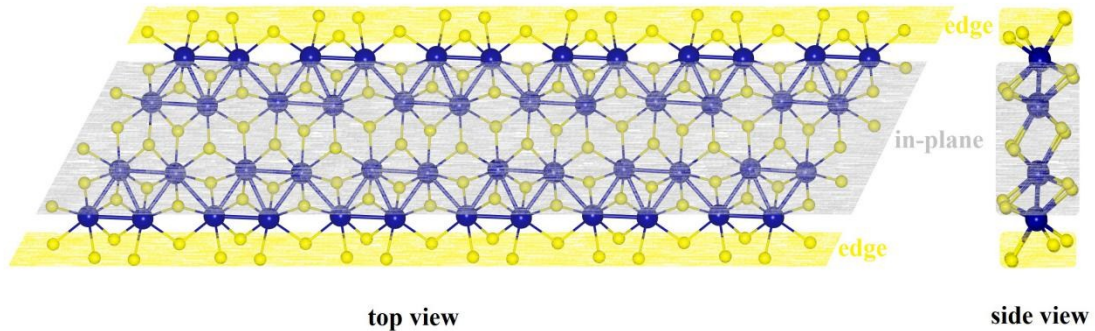


Fig. S1. Top and side views of a ReS₂ nanoribbons.

The calculated details of formation energy of TM-doped ReS₂

We calculate the formation energy (E_{form}), defined as

$$E_{\text{form}} = E_{\text{tot}}(\text{TM}) - E_{\text{tot}}(\text{ReS}_2) - \sum n_i \mu_i, \quad (1)$$

where $E_{\text{tot}}(\text{TM})$ and $E_{\text{tot}}(\text{ReS}_2)$ represent total energy of the doped and undoped ReS₂, n_i is the number of atoms that has been added to or removed from the supercell. μ_i is the chemical potential of species i (host or dopant atoms in the bulk phase). Because μ_{host} is greatly depended on experimental growth conditions, we consider the Re-rich and the S-rich conditions, the chemical potential of Re and S under Re-rich conditions can be defined as

$$\mu_{\text{Re}}^{\text{Re-rich}} = \mu_{\text{Re}}, \quad \mu_{\text{S}}^{\text{Re-rich}} = \mu_{\text{S}} + \frac{1}{2} \Delta H_f(\text{ReS}_2), \quad (2)$$

In which, μ_{Re} is the cohesive energy of Re at bulk metallic face-centered-cubic (fcc) structure, μ_{S} is the binding energy of S₂ molecule. Under S-rich conditions,

$$\mu_{\text{Re}}^{\text{S-rich}} = \mu_{\text{Re}} + \Delta H_f(\text{ReS}_2), \quad \mu_{\text{S}}^{\text{S-rich}} = \mu_{\text{S}}, \quad (3)$$

Where, $\Delta H_f(\text{ReS}_2)$ is the heat of formation of ReS₂ and defined as

$$\Delta H_f(\text{ReS}_2) = \mu_{\text{ReS}_2} - \mu_{\text{Re}} - 2\mu_{\text{S}}, \quad (4)$$

Where, μ_{ReS_2} is equal to $E_{\text{tot}}(\text{ReS}_2)$ per ReS₂ formula unit.

The adsorption free energy of hydrogen in TM-doped ReS₂

Hydrogen adsorption free energy (ΔG_{H^*}) can be defined as

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H, \quad (5)$$

where ΔE_{ZPE} is the difference in zero-point energy of hydrogen vibration between the adsorbed state and the gas phase, T is the surface temperature, ΔS_H is the entropy difference between the adsorbed state of the system and gas phase at standard condition, with $\Delta E_{ZPE} - T\Delta S_H = 0.24$ eV at $T = 300$ K, a reasonable, well established approximation.¹⁻³ With these values, ΔG_{H^*} can be rewritten as:

$$\Delta G_{H^*} = \Delta E_H + 0.24, \quad (6)$$

$$\Delta E_H = E(\text{ReS}_2 + \text{H}) - E(\text{ReS}_2) - E(\text{H}_2)/2, \quad (7)$$

where $E(\text{ReS}_2 + \text{H})$ and $E(\text{ReS}_2)$ are the energies of pristine or doped ReS₂ with and without an adsorbed H atom, $E(\text{H}_2)$ is the energy of a hydrogen molecule in the gas phase.

Table S1. The adsorption free energy of hydrogen (ΔG_{H^*} in eV), the bond length of S-H d_{S-H} (Å) and bader charges of S at different six sites for pure and TM-doped ReS₂.

		1	2	3	4	5	6
Pure ReS ₂	ΔG_{H^*}	1.45	1.64	1.60	1.67	1.65	1.78
	d_{S-H} (Å)	1.363	1.390	1.392	1.375	1.397	1.411
	q_{bader}	6.532	6.450	6.468	6.469	6.452	6.416
Mo-doing	ΔG_{H^*}	-0.01	0.61	0.25	0.22	0.61	0.85
	d_{S-H} (Å)	1.359	1.372	1.366	1.366	1.371	1.379
	q_{bader}	6.562	6.491	6.501	6.516	6.479	6.441
Cr-doing	ΔG_{H^*}	0.00	0.68	0.28	0.25	0.65	0.95
	d_{S-H} (Å)	1.362	1.372	1.368	1.367	1.372	1.377
	q_{bader}	6.541	6.509	6.474	6.501	6.467	6.464
Mn-doing	ΔG_{H^*}	0.72	1.22	0.73	0.89	0.98	1.07
	d_{S-H} (Å)	1.363	1.370	1.367	1.372	1.379	1.388
	q_{bader}	6.507	6.483	6.433	6.470	6.447	6.430
Fe-doing	ΔG_{H^*}	0.58	0.91	0.65	0.95	0.72	0.88
	d_{S-H} (Å)	1.365	1.369	1.367	1.371	1.381	1.392
	q_{bader}	6.475	6.485	6.412	6.436	6.432	6.438
Co-doing	ΔG_{H^*}	0.15	0.62	0.53	0.39	0.44	0.42
	d_{S-H} (Å)	1.362	1.363	1.366	1.367	1.379	1.386
	q_{bader}	6.484	6.463	6.441	6.436	6.411	6.403
Pt-doing	ΔG_{H^*}	0.18	0.01	0.59	0.15	0.34	0.12
	d_{S-H} (Å)	1.364	1.375	1.385	1.375	1.382	1.387
	q_{bader}	6.390	6.462	6.333	6.405	6.38	6.401
Au-doing	ΔG_{H^*}	0.10	0.78	0.29	0.41	0.25	0.24
	d_{S-H} (Å)	1.358	1.362	1.363	1.362	1.371	1.378
	q_{bader}	6.463	6.318	6.456	6.376	6.373	6.384
Ag-doing	ΔG_{H^*}	0.07	0.32	0.16	0.34	0.36	0.28
	d_{S-H} (Å)	1.360	1.366	1.364	1.66	1.373	1.380
	q_{bader}	6.517	6.405	6.472	6.431	6.383	6.386

The comparison of ΔG_{H^*} in ML-ReS₂ and ML-MoS₂

As shown in Fig. S2, for ML-ReS₂, the ΔG_{H^*} on different S atoms near the Re atom is different owing to the intrinsic asymmetry in 1T'-ReS₂. On the contrary, the ΔG_{H^*} is equal in ML-MoS₂ contributing from its high symmetric structural properties. Additionally, ΔG_{H^*} ranges from 1.45 to 1.78 eV in ML-ReS₂, which is lower than that of ML-MoS₂ with ΔG_{H^*} of 1.91 eV, indicating ReS₂ exhibits higher catalytic activity.

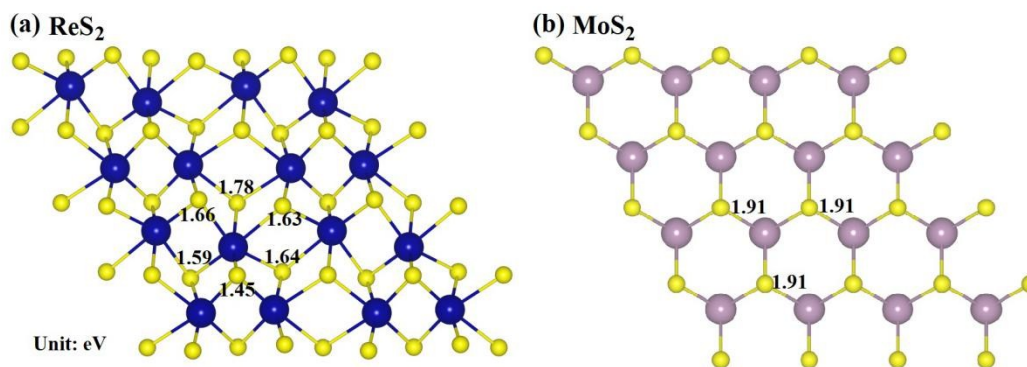


Fig. S2. The calculated ΔG_{H^*} on different S sites for (a) ML-ReS₂ and (b) ML-MoS₂.

SUPPORTING REFERENCES

1. Q. Wang, Z. L. Zhao, S. Dong, D. He, M. J. Lawrence, S. Han, C. Cai, S. Xiang, P. Rodriguez, B. Xiang, Z. Wang, Y. Liang, M. Gu, *Nano Energy*, 2018, **53**, 458.
2. J. K. Norskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandalov, U. Stimming, *Journal of the Electrochemical Society*, 2005, **152** J23.
3. Y. Zhou, W. Chen, P. Cui, J. Zeng, Z. Lin, E. Kaxiras, Z. Zhang, *Nano Lett.* 2016, **16**, 6058